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(54) Improvements relating to chemical compounds.

(57) The excessively fast reaction time produced by using polyoxyalkylene polyamines as curing agents for polyurethane formation can be moderated by reacting the polyoxyalkylene polyamines (1), with (2) derivatives of acrylic acid or alpha-substituted acrylic acids having terminal hydroxy groups, or with (3) compounds having oxirane rings. Alternatively the reaction product of (1) and (2) can be further reacted with (3), or the reaction product of (1) and (3) can be further reacted with (2). Preferred reactants are:

- (1) polyoxypropylene diamines and triamines, and polyoxyethylene bis propylene diamines;
- (2) hydroxyethyl acrylate, methacrylate or alphacyanoacrylate, and diethylene glycol monoacrylate; and
- (3) ethylene oxide, propylene oxide, n-butylglycidyl ether and styrene oxide.

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IMPROVEMENTS RELATING TO CHEMICAL COMPOUNDS

This invention relates to novel polyoxyalkylene polyamine-based curing agents for polyurethane preparation having improved reactivity toward isocyanates, and a gel time of convenient length and to their use in a process for making polyurethane, using such agents without any accelerators.

It is already known that polyoxyalkylenepolyamines can be used as curing agents when polyurethanes are manufactured from a polyisocyanate and a polyol (e.g. Japanese Official Bulletin Patent Publication 49-28914). However, polyoxyalkylenepolyamines are unsatisfactory curing agents because of their extremely high reactivity with isocyanates.

Although a method for lowering the reactivity of the amine with isocyanates by adding thereto a cyanoalkyl group or a alkyleneoxide group was proposed in Japanese Official Bulletin Patent Publication Sho. 49-28914 and U.S. Patent No. 4,075,130, the resulting products had insufficient solubility in polyols.

The literature on the Michael-type addition reaction feature of this invention includes:

Ogata and Asahara, Bull Chem. Soc. Japan, 39, 1486-1490 (1966);

Sanui and Ogata, Bull Chem. Soc. Japan, 1727 (1967); and Ogata, High Polymer Chemistry, 27, 1-19, (1970).

None of these, however, disclose in any manner Applicants' novel curing agents and process for using same.

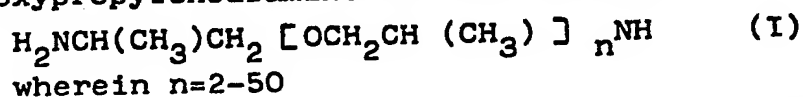
The present invention provides polyoxyalkylene-polyamine-based curing agents for making polyurethanes comprising reaction products of: (1) a polyoxyalkylene-polyamine, with (2) a derivative of acrylic acid or an alpha-substituted acrylic acid having a terminal hydroxyl group; or (3) a compound having an oxirane ring, or reaction products of (1) and (2) with (3),

or reaction products of (1) and (3) with (2).

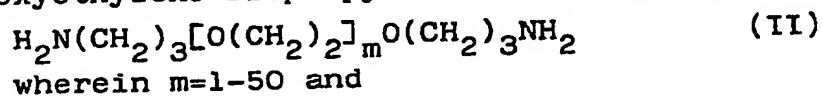
The invention also provides a process for making polyurethanes without using any accelerator which comprises adding to a polyol 5 to 100 percent by weight of at least of the above curing agents; condensing with an isocyanate and recovering the product so formed.

The preferred polyoxyalkylenepolyamines used in this invention include:

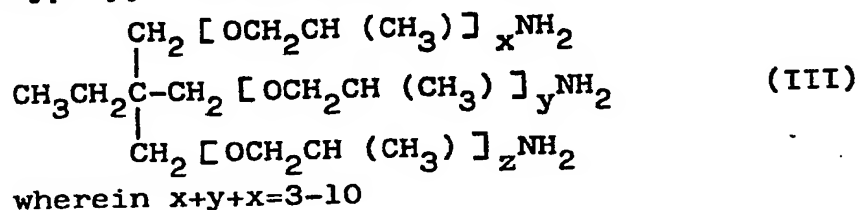
polyoxypropylenediamines of the formula



polyoxyethylene bispropylenediamines of the formula

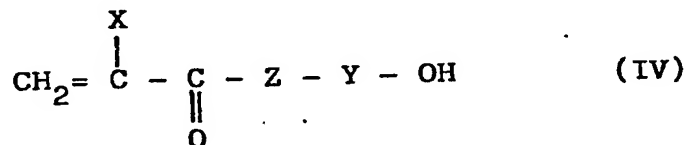


polyoxypropylenetriamines of the formula



The polyoxyalkylenepolyamine of formulae (I) and (III) are preferred. The preferred compounds of formula (I) have $n=2.6$, $n=5.6$ or $n=33.1$. The preferred compounds of formulae (II) and (III) are those where $m=2$ and $x+y+z=5.3$, respectively.

The preferred acrylic and alpha-substituted acrylic acid derivatives (2) are derivatives of acrylic acid, methacrylic acid and alpha-cyanoacrylic acid having the formula (IV):



wherein $\text{X}=\text{H}$, $-\text{CH}_3$, or $-\text{CN}$;

Y = alkylene, polyoxyalkylene or poly(alkyleneimine);

and

$\text{Z} = -\text{O}-$, $-\text{NH}-$ or $-\text{N}-\text{Y}-\text{OH}$

Exemplary compounds of formula (IV) include acrylates, methacrylates, alpha-cyanoacrylates, N-substituted acrylamides, N-substituted methacrylamides, N-substituted alpha-cyanoacrylamides, (and corresponding
5 N, N-bis-substituted amides) having hydroxyethyl, hydroxypropyl, hydroxybutyl, polyoxyethyleneglycol, polyoxypropyleneglycol and hydroxyethyliminoethyl groups.

Of these, the preferred compounds for use in
10 this invention are hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxyethyl cyanoacrylate and diethylene-glycol monoacrylate.

The reaction between the polyoxyalkylenepolyamine (1) and the acrylate (2) produces a Michael-type
15 reaction adduct, as shown by I.R. spectroscopy. This reaction can be carried out with a solvent, such as an alcohol (e.g. butanol), ether (e.g. dioxane), an aromatic hydrocarbon (e.g. toluene or o-xylene) or an aliphatic hydrocarbon, e.g., in an amount equal
20 to 10-80% of the charge reaction.

The mixture may be heated as required. The Michael adduct of the polyoxyalkylenepolyamine and the alpha-substituted acrylic acid derivative is produced almost quantitatively. Even if a small
25 quantity of unreacted compounds is contained, it does not adversely affect polyurethane curing. Preferably the content of unreacted material should not exceed 1% of the curing agent.

Unreacted acrylate and solvent (when used) can
30 be removed by azeotroping. To minimize the amount of unreacted acrylate in the product, an amount of acrylate close to the theoretical should be used.

The reaction temperature is generally less than 200°C and the stirring time is approx. 48 hours.
35 Where an alphacyanoacrylic acid derivative is used as the acrylic acid derivative (2), it sometimes generates heat and therefore, cooling is necessary in such case. The molar ratio of polyoxyalkylenepoly-

amine (1) and acrylic acid derivative (2) used is generally in the range of 5:1 to 1:5, preferably 3:1 to 1:3.

Preferably the oxirane compound has the formula

5 (V)



10

wherein R' is hydrogen, alkyl, aryl, hydroxyalkyl, alkoxyalkyl or hydroxyalkaryl.

Suitable epoxy compounds include ethylene oxide, propylene oxide, n-butylglycidyl ether and styrene oxide.

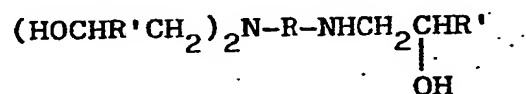
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A typical reaction between polyoxyalkylenepolyamine (1) and oxirane compound (2) proceeds as follows:

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+



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wherein

R = polyoxyalkylene, and R' has the meaning given above.

The preferred parameters for the reaction of polyamine (1) with oxirane compounds (2) are as follows:

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a) Reactants, molar ratios;

polyamine (diamine type)/oxirane
= 1/1.5 to 1:3.8 mol ratio (optimum range: 1:2 to 1:3.5 mol ratio)

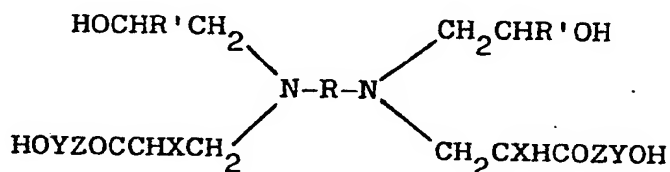
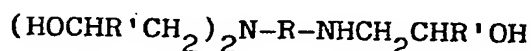
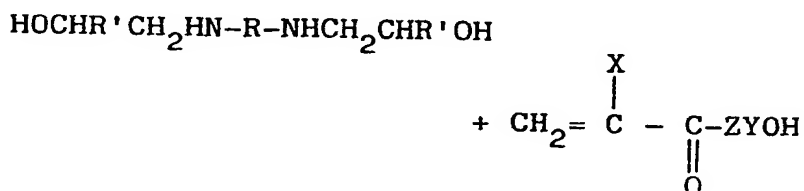
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polyamine (triamine type)/oxirane
= 1:2 to 1:5.5 mol ratio (optimum range: 1/3 to 1:4.5 mol ratio)

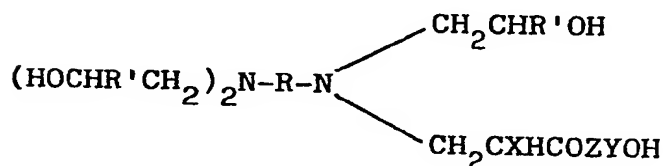
b) Reaction temperature: room temp. - 200°C
(optimum range 60 - 150°C)

c) Reaction time: 30 minutes - 48 hours
(optimum range 1 - 20 hours)

The reaction between (polyamine + oxirane compound)
+ acrylate proceeds as follows:



+



R = polyoxyalkylene; R', X, Y and Z are as above.

The preferred reaction parameters for above reaction are as follows:

- | | | |
|----|-------------------------|---|
| a) | Reactants, molar ratio: | polyamine oxirane compound/
acrylate = 1/1 to 1:4 mol
ratio (optimum range 1:2 to
1:3.5 mol ratio) |
| b) | Reaction temperature: | room temp. to 200°C
(optimum range: 60°C to
150°C) |
| c) | Reaction time: | 1 to 48 hours
(optimum range: 3 to 20 hours) |

The reaction parameters for the reaction between the polyamine (1), acrylate (2) and oxirane (3) reactants are substantially as above indicated for the polyamine, oxirane and acrylate reactants.

5 Unreacted acrylate and solvent (when used) can be removed by azeotroping. To minimize the amount of unreacted acrylate in the product, an amount of acrylate close to the theoretical should be used.

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The invention is illustrated in non limiting fashion by the following Examples. The "reference" Examples show the use of the various curing agents in making polyurethane.

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EXAMPLES 1-3

One mol of each polyoxypropylenediamine having the molecular weight shown in Table 1 was put in a 3-liter roundbottom flask. Then, 2 mols of hydroxyethylacrylate was added slowly, while stirring at temperature of 100°C. After the addition, the mixture was further stirred for 10 hours, so that a Michael addition reaction took place. The yield of adduct of polyoxypropylenediamine and hydroxyethylacrylate in each reaction product is shown in Table 1 and is nearly quantitative.

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<u>Table 1</u>		
Examples	Molecular weight of polyoxypropylene-diamine	Yield of Michael Adduct
1	230	98%
2	400	98%
25 3	2000	95%

EXAMPLE 4

Except for the use of one mol of polyoxypropylene-triamine (400g) having molecular weight 400 in lieu of one mol (230g) of polyoxypropylenediamine having

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molecular weight of 230, and 3 mols (348g) of hydroxyethylacrylate, the procedure of Example 1 was repeated. The yield of adduct of polyoxypropylenetriamine and hydroxyethylacrylate was 98%.

Reference Examples 1-4

0.023 mol of the compounds of Ex. 1-4 was put in a 500-ml roundbottom flask. Then, 0.05 mole of polypropyleneglycol having a molecular weight of 2,000 was added with 0.1 mol of tolylenediisocyanate. This mixture was stirred and blended at room temperature. The time required until gel of the mixture was measured as an indicator of reactivity with isocyanate. The results are shown in Table 2.

Except for using 0.023 mol of polyoxypropylenediamine having molecular weight of 230 instead of 0.023 mol of compound shown in Example 1 for comparison, the procedure was repeated, measuring the gel time.

Table 2

Reference Examples	Curing Agent Compound	Gel time (minute)
1	Example 1	15
2	Example 2	22
3	Example 3	28
4	Example 4	20
Control 1	Polyoxypropylenediamine (MW 230)	8 seconds

Example 5

One mole of polyoxypropylenediamine having molecular weight shown in Table 3 was put in a 3-liter round-bottom flask. Then, 2 mols (260g) of.

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hydroxyethylmethacrylate was dropped little by little while being stirred at temperature of 100°C. After the completion of the addition, the mixture was stirred for 10 hours, so that Michael addition reaction took place. The yield of an adduct of polyoxypropylenediamine and hydroxyethylmethacrylate in each reaction product is shown in Table 3.

Table 3

Example	Molecular weight of propylenediamine	Yield of Michael Adduct
5	230	98%
6	400	98%
7	2000	98%

Example 8

Except for using one mol (400g) of polyoxypropylenetriamine having molecular weight of 400 instead of one mole (230g) of polyoxypropylenediamine having molecular weight of 230, and 3 mols (390g) of hydroxyethylmethacrylate, the procedure of Ex. 5 was repeated. The yield of an adduct of polyoxypropylenetriamine and hydroxyethylmethacrylate in the reaction product was 98%.

Reference Examples 5-8

0.02 mol of the curing agent of Examples 5-8 was put in a 500ml round-bottom flask. Then 0.06 mol of polypropyleneglycol having a molecular weight of 2,000 was added with 0.1 mol of tolylenediisocyanate. The mixture was stirred and blended at room temperature and gel time was measured. The gel time is shown in Table 4.

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Excepting for the use of 0.02 mol of polyoxypropylenetriamine (Jeffamine T-403)

in lieu of 0.02 mol of curing agent compound shown in Example 5 for comparison, the procedure of Ref. Ex. 5 was repeated. The gel time is shown in Table 4.

Table 4

Reference Example	Curing agent compounds	Gel time (minute)
5	Example 5	17
6	Example 6	23
7	Example 7	28
8	Example 8	21
Control	Polyoxypropylenetriamine (MW 400)	15 seconds

Examples 9-11

One mol of polyoxypropylenediamine having molecular weight shown in Table 5 was put in a 3-liter round-bottom flask. Then 2 mols (282g) of hydroxyethyl-alpha-cyanoacrylate was dropped little by little while being stirred at temperature of 80°C. After the completion of the addition, the mixture was stirred for 10 hours, so that a Michael addition reaction took place. The yield of an adduct of polyoxypropylenediamine and hydroxyethyl-alpha-cyanoacrylate is shown in Table 5.

Table 5

Example	Molecular weight of polyoxypropylene-diamine	Yield of Michael adduct
9	230	100%
10	400	100%
11	2000	100%

Example 12

Except for the use of one mol (400g) of polyoxypropylenetriamine instead of one mol (230g) of polyoxypropylenediamine having molecular weight of 230, and 3 mols (423g) of hydroxyethyl-alphacyanoacrylate ester, the procedure of Ex. 9 was repeated. The yield of an adduct of polyoxypropylenetriamine and hydroxyethyl-alphacyanoacrylate in the reaction product was 100%,

Reference Example 9-12

0.02 mol of the curing agent of Examples 9-12 was put in a 500ml round-bottom flask. Then, 0.06 mol of polypropyleneglycol having molecular weight of 400 was added with 0.1 mol of hydrogenated diphenylmethanediisocyanate. The mixture was stirred and blended at room temperature, and gel time was measured. The gel time is shown in Table 6.

Except for the use of 0.02 mol of polyoxypropylenediamine having molecular weight of 2,000 instead of 0.02 mol of curing agent compound of Example 9 for comparison, the procedure of Ref. Ex. 9 was repeated. The gel time is shown in Table 6.

Table 6

Reference Examples	Curing agent compound	Gel time (minute)
9	Example 9	17
10	Example 10	22
11	Example 11	28
12	Example 12	21
Control 3	Polyoxypropylenediamine (MW 2000)	18 seconds

Examples 13-15

one mol of polyoxypropylenediamine having the molecular weight shown in Table 7 was put in a 3-liter round-bottom flask. Then, 2 mols (320g) of diethyleneglycolmonoacrylate was dropped little by little while being stirred at temperature of 100°C. After the completion of the addition, the mixture was further stirred for 10 hours, so that Michael addition reaction took place. The yield of an adduct of polyoxypropylenediamine and diethyleneglycolmonoacrylate in each reaction product is shown in Table 7.

Table 7

Examples	Molecular weight of polyoxypropylene-diamine	Yield of Michael adduct
13	230	98%
14	400	98%
15	2000	95%

Example 16

Excepting the use of one mol (400g) of polyoxypropylenetriamine instead of one mol (230g) of polyoxypropylenediamine having molecular weight of 230 and 3 mols (480g) of diethyleneglycolmonoacrylate ester, the procedure of Example 13 was repeated. The yield of an adduct of polyoxypropylenetriamine and diethyleneglycolmonoacrylate in the reaction product was 98%.

Examples 17-19

One mol of polyoxypropylenediamine having the molecular weight shown in table 8 was put in a 3-liter round-bottom flask. Then, 2 mols (230g) of

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N-hydroxyethylacrylamide was dropped little by little while being stirred at 100°C. After the completion addition, the mixture was further stirred and blended for 10 hours, so that Michael addition reaction took place. The yield of an adduct of polyoxypropylenediamine and N-hydroxyethylacrylamide for each reaction product is shown in Table 8.

Table 8

Examples	Molecular weight of polyoxypropylene-diamine	Yield of Michael adduct
17	230	98%
18	400	98%
19	2000	95%

Example 20

Excepting the use of one mol (400g) of polyoxypropylenetriamine having molecular weight of 400 in lieu of one mol (230g) of polyoxypropylenediamine having molecular weight of 230, and N-hydroxyethylacrylamide (345g), the procedure of Example 17 was repeated. The yield of an adduct of polyoxypropylenetriamine and N-hydroxyethylacrylamide in the reaction product was 98%.

Examples 21-23

One mol of polyoxypropylenediamine having molecular weight shown in Table 9 was put in a 3-liter round-bottom flask. Then, 2 mols (318g) of N, N-bis (hydroxyethyl) acrylamide were dropped little by little while being stirred at temperature of 100°C. After the completion of the addition, the mixture was stirred for 10 hours, so that Michael addition reaction took place. The yield of an adduct of polyoxypropylenediamine and N, N-bis

(hydroxyethyl) acrylamide in each reaction product is shown in Table 9.

Table 9

Examples	Molecular weight of polyoxypropylene-diamine	Yield Michael adduct
21	230	98%
22	400	98%
23	2000	90%

Reference Examples 6-7

The 0.02 mol of curing agent compounds shown in Examples 19 and 23 was put in a 500ml round-bottom flask. Then, 0.06 mol of polypropyleneglycol having molecular weight of 2,000 was added and further with 0.1 mol of tolylenediisocyanate. The mixture was stirred and blended at room temperature and gel time was measured. The results are shown in Table 10.

Except for the use of 0.02 mol of polyoxypropylenediamine having molecular weight of 2,000 in lieu of 0.02 mol of curing agent of Example 19 for comparison, the procedure of Reference Example 6 was repeated. The gel time is shown in Table 10.

Table 10

Reference Examples	Curing agent compound	Gel time
6	HEAA/D 2000 (Example 19)	35 minutes
7	BHEAA/D 2000 (Example 23)	40 minutes
Control 4	Polyoxypropylenediamine (MW 2000)	18 seconds

Examples 24-26

One mol of each polyoxypropylenediamine having the molecular weights shown in Table 11 was put into a 3-liter round-bottom flask. Then, 2 mols (258g) of N-hydroxyethylmethacrylamide was added to each flask while stirring at 100°C. After completing the addition, the mixture was stirred for 10 hours and heated at 120°C, to cause a Michael addition reaction to occur. The yield of an adduct of each polyoxypropylenediamine and N-hydroxyethylmethacrylamide in each example is shown in Table 11.

Table 11

Examples	Molecular weight of polyoxypropylene-diamine	Yield of Michael adduct
24	230	98%
25	400	95%
26	2000	90%

Examples 27-29

One mol of polyoxypropylenediamine having molecular weight shown in Table 12 was put in a 3-liter round-bottom flask. Then, 2 mols (280g) of N-hydroxyethyl-alpha-cyanoacrylamide was dropped little by little while being stirred at 80°C. After the completion of the addition, the mixture was further stirred for 10 hours, so that Michael addition reaction took place. The yield of an adduct of amine and N-hydroxyethyl-alpha-cyanoacrylamide in each reaction product is shown in Table 12.

Table 12

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Examples	Molecular weight of polyoxypropylene-diamine	Yield of Michael adduct
27	230	100%
28	400	100%
29	2000	98%

Example 30

One mol (400g) of polyoxypropylenetriamine having molecular weight of 400 was put in a 3-liter round-bottom flask. Then, 3 mols (420g) of N-hydroxyethyl-alpha-cyanoacrylamide were dropped little by little while being stirred at 80°C. After the completion of the drop, the mixture was further stirred for 10 hours, so that Michael addition reaction took place. The yield of an adduct in the reaction product was 100%.

Example 31

Using bis (aminopropyl) polyoxyethyleneglycol ether instead of polyoxypropylenediamine, the procedure of Example 9 was repeated. The yield of adduct was 98%.

Example 32-34

One mol of polyoxypropylenediamine having molecular weight shown in Table 13 was put in a 3-liter round-bottom flask. Then, it was heated at 140°C under nitrogen and 3 mols of n-butylglycidylether were slowly added. After the completion of the addition, the mixture was subjected to reaction for 2 hours. Unreacted n-butylglycidylether was evaporated under reduced pressure and a polyoxypropylenediamine n-butylglycidylether adduct was obtained.

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The hydroxyl value of each reaction adduct is shown in Table 13.

Table 13

Examples	Polyoxypropylene (molecular weight)	Hydroxyl value of adduct (KOH mg/g)	Code
32	230	237	nBGE/D-230
33	400	178	nBGE/D-400
34	2000	54	nBGE/D-2000

Example 35

Except for the use of one mol (400g) of polyoxypropylenetriamine having molecular weight of 400 instead of one mol (2,000g) of polyoxypropylenediamine having molecular weight of 2,000, and 4 mols (520g) of n-butylglycidylether, the procedure of Examples 32-34 was repeated. The hydroxyl value of obtained polyoxypropylenetriamine n-butylglycidylether reaction adduct (code: nBGE/T-403) was 221 KOHmg/g.

Example 36-38

One mol (2,280g) of the product of Example 34 was put in a 5-liter round-bottom flask. Then, it was heated at 100°C under nitrogen and 2.5 mols of hydroxyethylacrylate was dropped little by little. After the completion of the addition, the mixture was subjected to further reaction for 5 hours. After the end of reaction, the unreacted acrylate was evaporated under reduced pressure and the acrylate adduct was obtained. The results of each reaction product are shown in Table 14.

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Table 14

Examples	nBGE adduct	Function-ality ¹⁾	Average molecular weight	hydroxyl value (KOHmg/g)	Code
36	nBGE/D-230	4	720	310	HEA/nBGE/D-230
37	nBGE/D-400	4	890	250	HEA/nBGE/D-400
38	nBGE/D-2000	4	2500	90	HEA/nBGE/D-200

1. Equivalent to imino or reactive hydrogen.

Example 39

Except for the use of one mole (680g) of "BGE/T 403 obtained in Example 35 and 3.75 mols (435g) of hydroxyethylacrylate, the procedure of Ex. 36-38 was repeated. The obtained adduct of n-BGE/T-403 and hydroxyethylacrylate (code HEA/nBGE/T-403) has a functionality of 6, a average molecular weight of 900 and a hydroxyl value of 370 KOHmg/g.

Reference Examples 8-11

0.1 mol of the curing agents of Examples 36-39 was put in a 500-ml round-bottom flask. Then, 0.2 mol of tolylenediisocyanate was added. The mixture was stirred and blended. Time required until the mixture was geled, was measured as an indicator of reactivity with isocyanate. The results are shown in Table 15.

Table 15

Reference Examples	Curing Compound	Gel time (minute)
8	HEA/nBGE/D-230 (Example 36)	15
9	HEA/nBGE/D-400 (Example 37)	30
10	HEA/nBGE/D-200 (Example 38)	35
11	HEA/nBGE/T-403 (Example 39)	18

The molar ratios forth curing compounds of table 15 were:

HEA/nBGE/D-230 (or D-400 or D-2000) = 1.84/2.16/1 (molar ratio) in reaction product 0046088

HEA/nBGE/T-403 = 2.76/3.24/1. (molar ratio)

Example 40

One mol (2,232g) of Michael-type adduct of polyoxypropylenediamine having molecular weight of 2,000 and hydroxyethylacrylate obtained in Example 3 was put in a 3-liter round-bottom flask. Then, it was stirred under nitrogen and heated at 100°C with 2.5 mol (325g) of n-butylglycidylether were dropped little by little. After the addition, the mixture was subjected to further reaction at the same temperature for 15 hours. After completion of the reaction, unreacted n-butylglycidylether was evaporated under reduced pressure, and afterward a final product was obtained. The same procedure was carried out also with Michael-type adduct of the other polyoxypropylenediamine and hydroxyethylacrylate having different molecular weight described in the above examples.

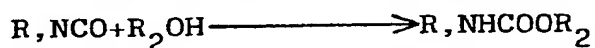
Reference Examples 12-13

0.05 mol of the curing agent compound of Example 40 was put in a 500ml round-bottom flask and 0.1 mol of tolylenediisocyanate was added. The mixture was stirred at room temperature and blended. The gel time was measured. The results are shown in Table 16. (No polyol is blended.)

Table 16

Reference Examples	Curing Agent Compound	Gel time (minute)
12	HEA/D-2000/n-butylglycidylether	35
13	(HEA/D-400/n-butylglycidylether)	(20)

The curing agents of the invention have utility as chain extenders for flexible urethanes, urethane latices and urethane encapsulation. They give the urethane product mechanical strength and elongation properties. The agents have improved solubility in polyols and improve cross-linking properties. The curing agents of the invention are useful in the preparation in known manner of polyurethanes by the condensation reaction of a polyisocyanate and a hydroxyl-group-containing material (polyol):



Polyols with which the curing agents of the invention can be used include for example, polyethyleneglycol having a molecular weight of approx. 200-600, and block polymers of polyethyleneglycol and polypropyleneglycol having a molecular weight of about 400-3000.

Isocyanates with which the curing agents of the invention can be used include tolylene diisocyanate, liquid diphenylmethane diisocyanate, and polymerized aromatic isocyanates.

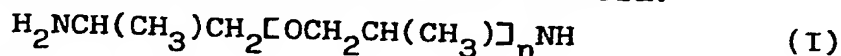
The curing agent according to the invention is used in a ratio of 5-100 weight percent, and preferably 10 to 20 weight percent, basis polyol.

CLAIMS:

1. Polyoxyalkylene polyamine-based curing agents for polyurethane preparation characterized in that they are the reaction products of (1) a polyoxyalkylene polyamine, with (2) a derivative of acrylic acid or an alpha-substituted acrylic acid having a terminal hydroxyl group, or (3) a compound having an oxirane ring, or a reaction product of (1) and (2) with (3), or a reaction product of (1) and (3) with (2).

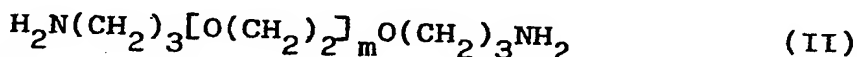
2. Curing agents according to Claim 1 characterized in that said polyoxyalkylene polyamine (1) is a

polyoxypropylenediamine of the formula:



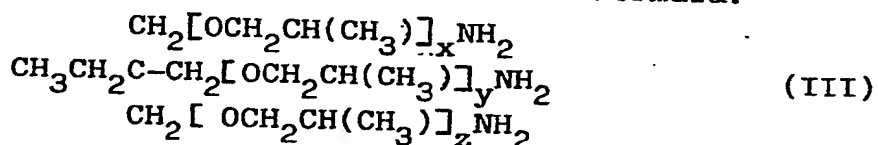
wherein $n=2-50$

a polyoxyethylene bispropylenediamine of the formula:



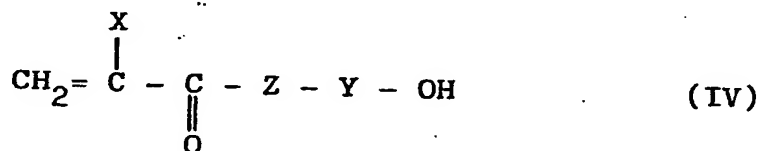
wherein, $m=1-50$ or

a polyoxypropylene triamine of the formula:



wherein $x+y+z=3-10$

3. Curing agents according to Claim 1 or 2 characterized in that said acrylic or substituted acrylic acid derivative (2) has the formula:



wherein $\text{X}=\text{H}$, $-\text{CH}_3$, or $-\text{CN}$;

Y = alkylene, polyoxyalkylene or poly(alkylene imine);
and

$\text{Z} = -\text{O}-$, $-\text{NH}-$ or $-\text{N}-\text{Y}-\text{OH}$

4. Curing agents according to any of Claims 1 to 3 characterized in that said compound having an oxirane ring (3) has the formula:



wherein R' is hydrogen, alkyl, aryl, hydroxy-alkyl, alkoxyalkyl or hydroxyalkaryl.

5. Curing agents according to any of Claims 1 to 4 characterized in that the molar ratio of polyoxyalkylene polyamine (1) to acrylic acid derivative (2) is from 5:1 to 1:5.

6. Curing agents according to any of Claims 1 to 4 characterized in that the molar ratio of (1) to (3) is from 1:1.5 to 1:5.5.

7. Curing agents according to any of Claims 1 to 4 characterized in that the molar ratio of reaction product of (1) and (3) with (2) is from 1:1 to 1:4.

8. Curing agents according to any of Claims 1 to 4 characterized in that the molar ratio of reaction product of (1) and (2) with (3) is from 1:1 to 1:4.

9. Curing agents according to any of Claims 1 to 8 characterized in that they also contain unreacted polyoxyalkylenepolyamine (1) and/or unreacted acrylic acid derivative (2).

10. The use of a curing agent according to any of Claims 1 to 9 in a process for preparing polyurethanes by condensing a polyisocyanate and a hydroxyl-containing compound, said curing agent being used in an amount of from 5 to 100 weight percent, based on said hydroxyl-containing compound.



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EUROPEAN SEARCH REPORT

0046088

Application number

EP 81 30 3660.5

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>DE - B - 1 917 408</u> (JEFFERSON CHEMICAL) * claim; column 2, lines 29 to 41 * & GB - A - 1 266 561 --	1,2, 4,10	C 08 G 65/32 C 08 G 18/50 C 08 G 18/32
X	<u>DE - A - 1 966 058</u> (JEFFERSON CHEMICAL) * claims 1, 6, 10; page 3 * & GB - A - 1 266 561 --	1,2, 4,10	
X	<u>DE - B2 - 1 966 059</u> (TEXACO) * claim; column 2, lines 40 to 53 * & GB - A - 1 266 561 -- <u>US - A - 3 666 788</u> (ROWTON) * column 1, lines 49 to 51 and formulas * --	1,4,10 2,10	TECHNICAL FIELDS SEARCHED (Int. Cl. ³) C 07 C 101/00 C 08 G 18/00 C 08 G 65/00
A	<u>DE - A1 - 2 721 626</u> (TEXACO) * claim 12; page 8, formula * & GB - A - 1 578 821 --		
A	<u>DE - A1 - 2 759 258</u> (HÜTTENES-ALBERTUS) * claims 1, 3 * --		CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
A	<u>DE - A1 - 2 809 977</u> (SERVA-ENTWICKLUNGS- LABOR) * page 3, formula * -- ./..		
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search Berlin		Date of completion of the search 13-11-1981	Examiner MARX

EPO Form 1503.1 08.78

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<p><u>GB - A - 1 419 154 (CIGA-GEIGY)</u></p> <p>* claim 1; page 6, lines 24 to 27, lines 36 to 38; page 7, lines 1 to 4 *</p> <p>-----</p>		
			TECHNICAL FIELDS SEARCHED (Int. Cl.)